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(21) International Application Number: PCT/EP97/07286 (22) International Filing Date: 22 December 1997 (22.12.97) (30) Priority Data: 08/773,524 23 December 1996 (23.12.96) US (71) Applicant (for all designated States except PL US): SAR-TOMER COMPANY, INC. [US/US]; Oaklands Corporate Center, 502 Thomas Jones Way, Exton, PA 19341 (US). (71) Applicant (for PL only): CRAY VALLEY S.A. [FR/FR]; Tour Total, 24, cours Michelet, F-92800 Puteaux (FR). (72) Inventors; and (75) Inventors/Applicants (for US only): CESKA, Gary, W. [US/US]; 310 Long Ridge, Exton, PA 19341 (US). FAN, Mingxin [CN/US]; 49 Sheffield Lane, West Chester, PA 19380 (US). HORGAN, James [US/US]; 805 Copeland School Road, West Chester, PA 19380 (US). (74) Agent: CHAILLOT, Geneviève; Cabinet Chaillot, 16-20, avenue de l'Agent Sarre, Boîte postale 74, F-92703 Colombes Cedex (FR).		(81) Designated States: CA, CN, JP, KR, MX, PL, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: UNSATURATED (METH)ACRYLATE ESTERS CONTAINING EPOXIDIZED CYCLIC GROUPS AND PROCESS FOR PREPARING (57) Abstract <p>A process of making compounds of formula (I), wherein Z is an unsubstituted or substituted n-valent cyclic moiety bearing at least one endocyclic oxirane group; Y is O, S, NH, (Ia) or (Ib); R² is a divalent linking group; X is O, S or NH; R¹ is H or (C₁-C₆) alkyl; and n is an integer from 1 to 6, Z being mono- to hexavalent respectively, it being possible for -Y-R² to represent a single bond, comprises reacting a compound of formula (II), wherein Z¹ is a cyclic moiety bearing at least one endocyclic C=C group; and Y, R², X, R¹ and n are as defined above with hydrogen peroxide in the presence of (a) tungstic acid or tungsten oxide or molybdic acid or a molybdenum oxide; (b) phosphoric acid or a salt thereof; and (c) at least one phase transfer catalyst.</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div style="text-align: center;"> $[Z-]_n - Y - R^2 - X - \overset{\overset{O}{\parallel}}{C} - \underset{\underset{R^1}{ }}{C} = CH_2 \quad (I)$ </div> <div style="text-align: center;"> $[Z^1-]_n - Y - R^2 - X - \overset{\overset{O}{\parallel}}{C} - \underset{\underset{R^1}{ }}{C} = CH_2 \quad (II)$ </div> </div>		

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UNSATURATED (METH)ACRYLATE ESTERS CONTAINING EPOXIDIZED CYCLIC GROUPS AND PROCESS FOR PREPARING.

This invention relates to epoxidation of unsaturated (meth)acrylate esters.

5 (Meth)acrylate monomers which have epoxide functional groups are widely used in industry as chemical intermediates for synthetic materials. Traditionally, these monomers are being produced from epichlorohydrin via coupling with corresponding salts. Epoxidation of unsaturated organic
10 substrates without (meth)acrylate functional groups is much easier due to the lack of (meth)acrylate functional group polymerization initiated by peroxide or radicals generated in situ. US 2,833,787 and 2,833,788 describe the epoxidation of nonconjugated ethylenic compounds by hydrogen peroxide and
15 water soluble sodium pertungstate at a pH of between 3 and 7. Similarly, unsaturated acids were epoxidized by hydrogen peroxide and sodium tungstate (J. Org. Chem., vol. 24, 54).

Olefin epoxidation using hydrogen peroxide and a water soluble alkali metal tungstate in the presence of a
20 phase transfer agent was reported (J. Org. Chem., vol. 48, 3831 and J. Org. Chem., vol. 50, 2688). Similarly, water-soluble molybdophosphoric and tungstophosphoric acid (hetero polyacids) were used in the catalytic epoxidation of olefins using hydrogen peroxide (J. Org. Chem., vol. 52, 1868 and
25 vol. 53, 3587).

The epoxidation of unsaturated (meth)acrylate esters using peracetic acid was described in US 3,459,775 in very low yield. US 5,283,360 describes the selective epoxidation of unsaturated (meth)acrylates using hydrogen
30 peroxide in the presence of water soluble alkali metal molybdates and tungstates as well as heteropolyacid for cyclic substrates and phase transfer agent. According to US 5,283,360, conversion was less than 100% and residual allylic compound was present.

35 US Patents 5,783,360 and 5,510,516 to Caubere et al, show epoxidation of unsaturated (meth)acrylate esters with hydrogen peroxide using a catalyst system which comprises

alkali metal salts of tungstic or molybdic acids and a heteropolyacid. Caubere et al do not show (meth)acrylates which have been alkoxylated, nor do they show phosphoric acid.

GB application 2 055 821 A by Venturello et al,
5 shows epoxidation of olefins with hydrogen peroxide using a catalyst system consisting of W, Mo, or V, and at least one derivative of P or As. This application does not show epoxidation of (meth)acrylates or alkoxylated compounds.

One of the problems of the prior art processes is
10 low catalyst lifetime and low catalytic conversion. Low conversion results in contamination with the starting material which causes crosslinking during free radical polymerization. Prior art catalytic systems include water soluble alkali metal salts of molybdates and tungstates as well as their
15 heteropolyacids. In the presence of phase transfer agent, the conversion is low and residual unsaturated (meth)acrylate remains in the initial product mixture, resulting in low stability and crosslinking in some applications. Prior art in this field requires water soluble alkali metal salts of
20 molybdates and tungstates and their heteropolyacids.

It is therefore an object of the present invention to provide an improved method of selectively epoxidizing compounds having acrylate or methacrylate groups.

It is also an object of the invention to provide
25 a new class of (meth)acrylates containing epoxide functionalities.

A further object of the invention is to provide a method of epoxidizing (meth)acrylates which have improved catalyst life and higher than previously achieved yields.

30 These objects, and others which will become apparent from the following disclosure are achieved by the present invention which comprises in one aspect a process for selectivity epoxidizing (meth)acrylate monomers using hydrogen peroxide as oxidizing agent and a catalyst system comprising
35 water insoluble tungstic acid or molybdic acid or molybdenum oxide in combination with phosphoric acid or a salt thereof in the presence of phase transfer agent.

Another aspect of the invention is a process for epoxidizing (meth)acrylate monomers which results in complete conversion comprising using insoluble tungstic acid or tungsten oxide (or molybdic acid or molybdenum oxide) and phosphoric acid or a metal salt thereof with or without any acidity adjustment.

The current invention will result in complete conversion of unsaturated (meth)acrylate esters to (meth)acrylate epoxides using insoluble tungstic acid or molybdic acid or molybdenum oxide and phosphoric acid or a metal salt thereof with or without any acidity adjustment.

The catalyst composition used in the process of the invention is highly effective and selective, which is very advantageous in the epoxidation of unsaturated (meth)acrylate monomers.

The new method involves low level of catalyst composition. Furthermore, no organic acid and/or peracid is used which results in simple product workup and process.

The present invention uses hydrogen peroxide in the presence of

- (a) tungstic acid or tungsten oxide or molybdic acid or a molybdenum oxide ;
- (b) phosphoric acid or a metal salt thereof ; and
- (c) at least one phase transfer catalyst.

The epoxidation of unsaturated (meth)acrylates with hydrogen peroxide in the presence of tungsten catalyst or molybdenum catalyst, phosphoric acid or its salt, and phase transfer catalyst can be performed at any temperature which is sufficient to react, however, particularly suitable temperatures are between 0°C and 100°C, preferably from 25°C to 70°C and more particularly from 50 to 70°C. The reaction takes place faster at higher temperature and requires shorter time to complete, the reaction is typically exothermic and slow addition of hydrogen peroxide is preferred to control the exotherm. At higher temperature, hydrogen peroxide undergoes decomposition. The reaction can be performed at pressures from subatmospheric to superatmospheric pressures ; however, the reaction is preferably carried out at atmospheric pressure.

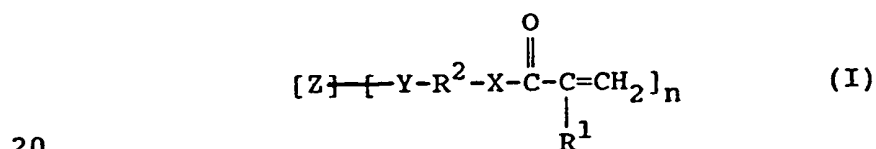
The epoxidation can be performed with or without solvent, solvent can be used to reduce the viscosity, if solvent is needed, a water-immiscible organic solvent such as chlorinated hydrocarbons, ethers, glycol ethers, aliphatic and aromatic hydrocarbons, alkyl esters, and combinations thereof. Particular suitable organic solvents are toluene, chlorobenzene, chloroform, methylene chloride, heptane, and the like.

Hydrogen peroxide solution is used as oxidant in the concentration in water of 5 to 70% by weight. The amount of hydrogen peroxide can vary depending on the desired degree of epoxidation, typically from 0.1 to 1.5, and particularly from 1 to 1.5, equivalent per C=C in Z¹ in the starting material.

The phase transfer catalyst can be used from 0.001 to 1.5, preferably 0.05 to 1.0, equivalent per equivalent of carbon carbon double bond in Z¹. Suitable phase transfer catalysts includes quaternary ammonium salts, quaternary phosphonium salts, polyethers and ether derivatives such as polycondensates of polyethers or functional polyethers, and the like. Examples of phase transfer catalysts include, for example, trioctylmethylammonium chloride, trioctylmethylammonium bromide, trioctylmethylammonium iodide, trioctylmethylammonium hydrogen sulfate, trioctylmethylammonium nitrate, tetrahexylammonium chloride, tetrahexylammonium bromide, tetrahexylammonium iodide, tetrahexylammonium hydrogen sulfate, tetrahexylammonium nitrate, tetrabutylammonium chloride, tetrabutylammonium bromide, tetrabutylammonium nitrate, tetrabutylammonium hydrogen sulfate, dioctadecyldimethylammonium chloride, dioctadecyldimethylammonium bromide, dioctadecyldimethylammonium nitrate, dioctadecyldimethylammonium hydrogen sulfate, dihexadecyldimethylammonium chloride, dihexadecyldimethylammonium bromide, dihexadecyldimethylammonium nitrate, dihexadecyldimethylammonium hydrogen sulfate, trioctylmethylphosphonium chloride, trioctylmethylphosphonium bromide, trioctylmethylphosphonium nitrate, trioctylmethylphosphonium hydrogen sulfate, tetrahexyl-

phosphonium chloride, tetrahexylphosphonium bromide, tetrahexylphosphonium nitrate, tetrahexylphosphonium hydrogen sulfate, tetrabutylphosphonium chloride, tetrabutylphosphonium bromide, tetrabutylphosphonium nitrate, tetrabutylphosphonium
 5 hydrogen sulfate, tetrabutylphosphonium iodide, dioctadecyldimethylphosphonium chloride, dioctadecyldimethylphosphonium bromide, dioctadecyldimethylphosphonium nitrate, dioctadecyldimethylphosphonium hydrogen sulfate, dihexadecyldimethylphosphonium chloride, dihexadecyldimethylphosphonium bromide,
 10 dihexadecyldimethylphosphonium nitrate, dihexadecyldimethylphosphonium hydrogen sulfate, tetraalkylammonium hydroxide, tetraalkylammonium tribromide, tetraalkylammonium trifluoromethanesulfonate, and any combination thereof.

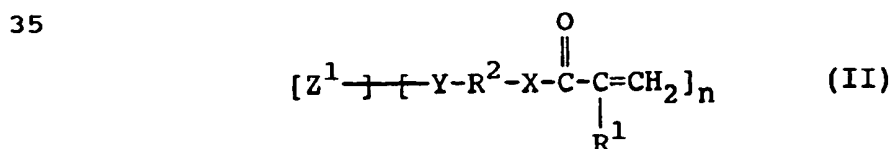
The method of the invention comprises a process
 15 of making compounds of the formula :



wherein :

- Z is an unsubstituted or substituted n-valent cyclic moiety bearing at least one endocyclic oxirane group;
- Y is O, S, NH, $-\overset{\overset{O}{\parallel}}{O}-C-$ or $-C-\overset{\overset{O}{\parallel}}{O}-$;
- 25 - R^2 is a divalent linking group ;
- X is O, S or NH ;
- R^1 is H or (C_1-C_6) alkyl ; and
- 30 - n is an integer from 1 to 6, Z being mono- to hexavalent respectively,

it being possible for $-Y-R^2-$ to represent a single bond, characterized by the fact that it comprises reacting a compound of the formula :



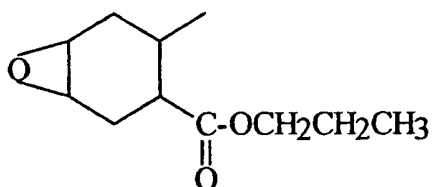
wherein :

- Z^1 is an unsubstituted or substituted n-valent cyclic moiety bearing at least one endocyclic C=C group ; and
- Y, R^2 , X, R^1 and n are as defined above,

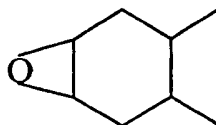
5 with hydrogen peroxide in the presence of :

- (a) tungstic acid or tungsten oxide or molybdic acid or a molybdenum oxide ;
- (b) phosphoric acid or a salt thereof ; and
- (c) at least one phase transfer catalyst.

10 Z may be an epoxidized dicyclopentenyl group or an epoxidized unsubstituted or substituted cyclohexenyl group. According to an embodiment of the present invention, the process leads to compound (I) wherein Z is



or to a compound (I) wherein Z is



15 or to a mixture of both.

The resultant compounds (I) are novel, except when Z is an epoxidized dicyclopentenyl group, Y is O, R^2 is C_1 - C_{10} alkylene, X is O, and R^1 is H or methyl.

Preferred compounds are those wherein R^1 is H or
 20 methyl, i.e., acrylates or methacrylates, and those wherein X is O and R^2 is an alkylene, or (poly)oxyalkylene having from 1 to 20 carbon atoms and more particularly alkylenes having from 2 to 12 carbon atoms or (poly)oxyalkylenes having from 4 to 20 carbon atoms.

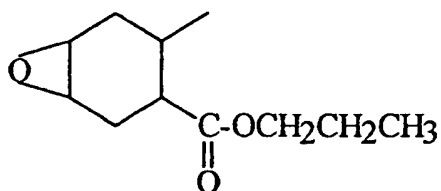
25 Especially preferred compounds (I) are those wherein Z is unsubstituted or substituted epoxidized cyclohexenyl groups. While any substituent can be used, preferred

30 one alkyl or ester, for example, methyl or $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$

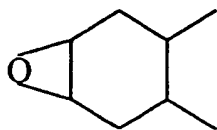
7

ester.

Compounds wherein Z =



or



can be cited.

Phosphoric acid or its various salts can be used from 0.001 to 0.5 equivalent per equivalent of carbon carbon double bond. Sodium or potassium salts of monobasic, dibasic or tribasic salts of phosphoric acid can also be used. The final pH can be adjusted by other acids or bases to a value between 0 and 5.

Tungstic acid or its metal salts can be used as the metal catalysts, the metal salts are water soluble and the acid is not. Molybdic acid or molybdenum oxide can also be used as metal catalyst. The typical catalyst is used from 0.005 to 1% and the preferred catalyst is tungstic acid which is not water-soluble or molybdic acid.

The epoxidized unsaturated (meth)acrylates can be used in a variety of applications, such as coatings, epoxy/amine cure, cationic cure, and chemical intermediates for polymers and oligomers.

One aspect of the invention is composition comprising compounds of formula (I) for use in the above-mentioned applications.

The compounds of formula (I) can be used to make novel polymers, both homo- and copolymers. Especially useful polymers are copolymers of a compound of formula I and one or more acrylates, methacrylates, epoxy compounds. Also preferred are copolymers of : (A) a compound of formula (I) ; (B) an epoxy compound not containing an acrylate or methacrylate group, and (C) an acrylate or methacrylate compound not containing an epoxy group.

The polymers can be prepared by exposing the monomer or monomer mixture to radiation according to methods known in the art.

In some embodiments, the monomers are first reacted
5 via free radical polymerization and then cured via the epoxy groups. In other embodiments the epoxy groups can be polymerized using cationic initiator.

A preferred embodiment is when both free radical initiator and cationic initiator are present and the mixture
10 is exposed to radiation to form a cured polymer.

The cured polymers can be used for coatings, sealants, adhesives, inks, and the like.

The following non-limiting examples are presented to illustrate a few embodiments of the invention. All parts
15 and percentages are by weight unless otherwise indicated.

EXAMPLE 1

Epoxidation of 2-(dicyclopentenylloxy)ethyl methacrylate

In a four-necked flask tungstic acid (1.50 g), sodium hydroxide (25%, 0.75 ml), and phosphoric acid (85%,
20 0.50 ml) were added, followed by addition of 2-(dicyclopentenylloxy) ethyl methacrylate (131.0 g, 0.5 mole), toluene (131.0 g), and trioctylmethyl ammonium chloride (1.50 g). The resultant mixture was stirred to form a yellow mixture and heated to 60°C, after which hydrogen peroxide (30%, 100.0 ml)
25 was added slowly over 50 min. The reaction mixture was stirred at 60°C for 2 ½ hours.

GC analysis showed no starting material left and 100% conversion to epoxide was obtained.

EXAMPLE 2Epoxidation of dicyclopentenyl methacrylate

Following the same procedure, dicyclopentenyl methacrylate was epoxidized with 100% conversion.

5

EXAMPLE 3Epoxidation of dicyclopentenyl acrylate

Following the same procedure, dicyclopentenyl acrylate was epoxidized with 100% conversion.

EXAMPLE 410 Epoxidation of 2-(dicyclopentenylloxy) ethyl methacrylate

Example 1 was repeated without sodium hydroxide. The material was epoxidized with 100% conversion.

EXAMPLE 5Synthesis of unsaturated methacrylate ester

15 In a four-necked flask, tetrahydrophthalic anhydride (152.1 g), hydroxyethyl methacrylate (130.0 g), and methoxyphenol (0.30 g) were added and stirred, and air sparge was applied while stirring. The mixture was heated to 100°C for six hours. IR showed no anhydride starting material left.

20 To the above product, 1-propanol (84.0 g), methoxyphenol (2.0 g), toluene (75.0 g), heptane (75.0 g), methanesulfonic acid (70%, 10.0 g) were added, air sparge applied, the mixture was stirred and refluxed. Water was removed azeotropically during the reaction and the
25 esterification reaction completed in 5.0 hours. The final mixture was neutralized and washed with 25% NaOH and solvent

was stripped at 3.33×10^3 Pa (25 mmHg) at 95°C. 273.0 g clear light yellow unsaturated methacrylate was obtained.

EXAMPLE 6

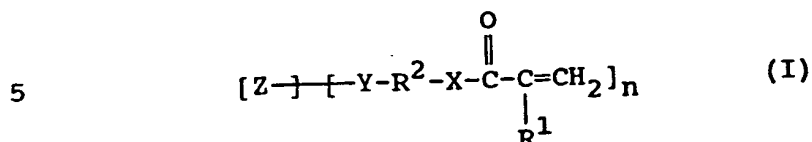
Epoxidation of unsaturated methacrylate ester from Example 5

5 100.0 g unsaturated methacrylate ester from Example 5, 100.0 g toluene, 0.80 g trioctylmethyl ammonium chloride, 0.80 g tungstic acid, 0.40 g sodium hydroxide (25%), and 0.40 g phosphoric acid (85%) were added to a reactor, and the mixture was stirred and heated to 60°C. Then 100 ml H₂O₂
10 (30%) was slowly added within 30 min. and the temperature was controlled at 60°C. The reaction mixture was kept at 60°C for additional 3 $\frac{1}{2}$ hours. The unsaturated methacrylate was completely epoxidized based on GC analysis.

While the invention has been described in sufficient
15 detail for those skilled in the art to make and use it, various modifications, alternatives, and improvements should become readily apparent without departing from the spirit and scope of the invention as set forth in the following claims.

CLAIMS

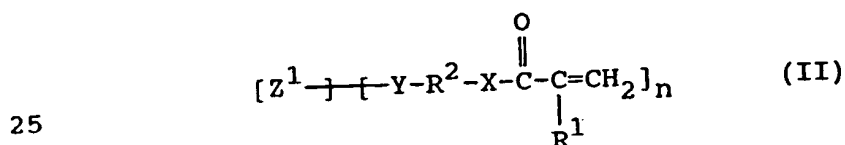
1 - Process of making compounds of the formula :



wherein :

- Z is a unsubstituted or substituted n-valent cyclic moiety bearing at least one endocyclic oxirane group ;
- 10 - Y is O, S, NH, $-\text{O}-\overset{\overset{O}{\parallel}}{C}-$ or $-\overset{\overset{O}{\parallel}}{C}-\text{O}-$;
- R^2 is a divalent linking group ;
- 15 - X is O, S or NH ;
- R^1 is H or (C_1-C_6) alkyl ; and
- n is an integer from 1 to 6, Z being mono- to hexavalent respectively,

it being possible for $-\text{Y}-R^2-$ to represent a single bond,
20 characterized by the fact that it comprises reacting a compound of the formula :

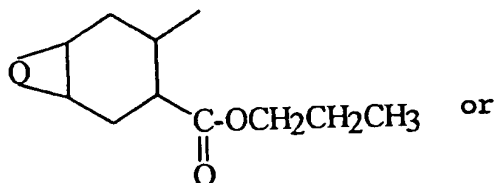


wherein :

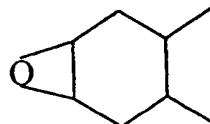
- Z^1 is a cyclic moiety bearing at least one endocyclic C=C group ; and
- 30 - Y, R^2 , X, R^1 and n are as defined above, with hydrogen peroxide in the presence of :
 - (a) tungstic acid or tungsten oxide or molybdic acid or a molybdenum oxide ;
 - (b) phosphoric acid or a salt thereof ; and
 - 35 (c) at least one phase transfer catalyst.

2 - Process according to claim 1, characterized by the fact that Z is an epoxidized dicyclopentenyl group or an epoxidized unsubstituted or substituted cyclohexenyl group.

3 - Process according to claim 2, characterized by the fact that leads to compound (I) wherein Z is



to a compound (I) wherein Z is



5 or to a mixture of both.

4 - Process according to anyone of claims 1 to 3, characterized by the fact that R^2 is an alkylene or (poly)alkylene group having from 1 to 20 carbon atoms, and particularly alkylene group having from 1 to 12 carbon atoms
10 and (poly)oxyalkylene groups having from 4 to 20 carbon atoms.

5 - Process according to anyone of claims 1 to 4, characterized by the fact that said hydrogen peroxide is introduced in an amount of about 1 to 1.5, particularly of about 1 to 1.5, equivalent per equivalent of C=C group in Z^1 .

15 6 - Process according to anyone of claims 1 to 5, characterized by the fact that the reaction is conducted at a temperature of about 0°C to 100°C.

7 - Process according to claim 6, characterized by the fact that the reaction is conducted at a temperature of about 25°C to 70°C, particularly at a temperature of about 50 to 70°C.

8 - Process according to anyone of claims 1 to 7, characterized by the fact that the phase transfer catalyst is present in an amount of about 0.001 to 1.5, particularly of about 0.05 to 1.0, equivalent per equivalent of C=C group in Z^1 .
25

9 - Process according to anyone of claims 1 to 8, characterized by the fact that the phase transfer catalyst is selected from the group consisting of quaternary ammonium salts, quaternary phosphonium salts, polyethers and polyether derivatives.
30

10 - Process according to anyone of claims 1 to 9, characterized by the fact that the reaction is conducted in the presence of a water immiscible organic solvent.

11 - Process according to claim 10, characterized
5 by the fact that the water immiscible organic solvent is selected from the group consisting of chlorinated hydrocarbons, ethers, glycol ethers, aliphatic and aromatic hydrocarbons, alkyl esters and combinations thereof, particularly from the group consisting of toluene,
10 chlorobenzene, chloroform, heptane and methylene chloride.

12 - Process according to anyone of claims 1 to 11, characterized by the fact that the phosphoric acid or phosphoric acid salt comprises about 0.001 to 0.5 equivalent per equivalent of C=C group in Z¹.

13 - Process according to anyone of claims 1 to 12,
15 characterized by the fact that the phosphoric acid salt is a sodium or potassium monobasic, dibasic, or tribasic phosphoric acid salt.

14 - Process according to anyone of claims 1 to 13,
20 characterized by the fact that the pH of the reaction is adjusted by acids or bases to a value between 0 and 5.

15 - Process according anyone of claims 1 to 14, characterized by the fact that the tungstic acid or tungsten oxide or molybdic acid or molybdenum oxide is present in an
25 amount of about 0.005 to 1% based on weight of compound of formula (II).

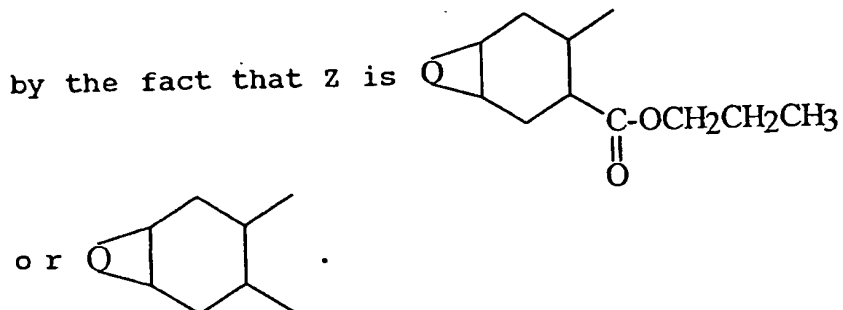
16 - Compound of formula (I) as defined in anyone of claims 1 to 4, except for compounds wherein Z is an epoxidized dicyclopentenyl group, Y is O, R² is C₁-C₁₀
30 alkylene, X is O, and R¹ is H or methyl.

17 - Compound of claim 16, characterized by the fact that R¹ is H or methyl.

18 - Compound of claims 16 or 17, characterized by the fact that X is O and R² is an alkylene or
35 (poly)oxyalkylene having a number of carbons from 1 to 20, such as an alkylene having from 1 to 10 carbon atoms or a (poly)oxyalkylene having from 4 to 20 carbon atoms.

19 - Compound of anyone of claims 16 to 18, characterized by the fact that Z is epoxidized cyclohexenyl group or epoxidized substituted cyclohexenyl group, such as epoxidized ester substituted or alkyl-substituted cyclohexenyl group.

20 - Compounds according to claim 19, characterized



21 - Composition comprising at least one compound as defined in anyone of claims 16 to 19 or obtained by a process as defined in anyone of claims 1 to 15.

22 - Composition comprising a polymer of a compound as defined in anyone of claims 16 to 19 or obtained by a process as defined in anyone of claims 1 to 15.

23 - Composition of claim 22, characterized by the fact that the polymer is a copolymer of a compound of formula (I) and one or more acrylates, methacrylates, epoxy compounds.

24 - Composition of anyone of claims 22 and 23, characterized by the fact that the polymer is prepared by exposing the compound and any comonomers to radiation.

25 - Composition of anyone of claims 22 to 24, characterized by the fact that the polymer is a copolymer of :

- (A) a compound of formula (I) ;
- (B) an epoxy compound not containing an acrylate or methacrylate group ; and
- (C) an acrylate or methacrylate compound not containing an epoxy group.

26 - Composition of claim 25, characterized by the fact that the polymer is prepared by exposing a mixture of (A), (B) and (C) to radiation in the presence of free radical initiator and cationic initiator.